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REVIEW ARTICLE

The nanotechnology among US: are metal and metal oxides nanoparticles a nano or mega risk for soil microbial communities?

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ABSTRACT

Metal nanoparticles and metal oxides nanoparticles (MNPs/MONPs) have been widely included in a great diversity of products and industrial applications and they are already a part of our everyday life. According to estimation studies, their production is expected to increase exponentially in the next few years. Consequently, soil has been suggested as the main sink of MNPs/MONPs once they are deliberately or accidentally released into the environment. The potential negative perturbations that may result on soil microbial communities and ecological processes are resulting in concerns. Several nano-toxicological studies of MNPs/MONPs, reported so far, have focused on aquatic organisms, animals, and soil invertebrates. However, during recent years, the studies have been oriented to understand the effects of MNPs/MONPs on microbial communities and their interaction with soil components. The studies have suggested that MNPs/MONPs are one of the most toxic type to soil biota, amongst different types of nanomaterials. This may threaten soil health and fertility, since microbial communities are known to support important biological processes and ecosystem services such as the nutrient cycling, whereby their protection against the environmental pollution is imperative. Therefore, in this review we summarize the actual knowledge available from the last five years (2013–2018) and gaps about the potential negative, positive or neutral effects produced on soil by different classes of MNPs/MONPs. A particular emphasis has been placed on the associated soil microorganisms and biological processes. Finally, perspectives about future research are discussed.

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Introduction

The production of metal nanoparticles and metal oxide nanoparticles (MNPs/MONPs) has experienced fascinating developments during the last decade, and their application in medicine, electronics, cosmetic, and textile industry is expanding. Moreover, MNPs/MONPs have been proposed as a new frontier in modern agriculture [1].

The significant applicability of MNPs/MONPs has mostly been attributed to their interesting enhanced physicochemical properties (e.g. high reactivity, better optical properties, and great surface area to volume ratio). However, this massive use of MNPs/MONPs has raised great concern due to their potential interaction with different compartments in the environment, which has been evident from several interesting reviews on this topic that have been published in later years [2–9].

Overall, a large number of nanotoxicological studies have been performed in aquatic organisms, such as daphnids, zebrafish, algae, fresh water bivalve, diatom, among others, providing an overview regarding the potential toxicity of MNPs/MNOPs. In this regard, some actual publications are listed in Table 1. As can be seen, studies with MNPs/MONPs frequently have evaluated toxicity mechanisms that are expressed, such as the production of reactive oxygen species (ROS), disruption of membranes, glutathione (GSH) levels, cytotoxicity, and enzyme activities, among other parameters [10].

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Table 1. Toxicity studies of metal and metal oxide nanoparticles to aquatic and terrestrial organisms reported on literature during the last five years (2013–2018).

Metal	Target Organism	Tested dose ($mg\ L^{-1}$-$mg\ Kg^{-1}$)	Parameters	Reference
TiO_2	*Artemia salina*	10	Trophic transfer of arsenic, superoxide dismutase (SOD) and acetylcholonesterase (AChE).	[10]
	Dunaliella tertiolecta	0.01–10	Growth inhibition, oxidative stress, reactive oxygen species (ROS) accumulation and chlorophyl content.	[11]
	Phaeodactylum tricornutum	2.5–40	Physiological and biochemical responses in 96 h growth tests in batch-culture.	[12]
	Daphnia magna	0.002–200	Median lethal concentration (LC_{50}) (8 h): 0.139, 0.778, and $>500\ mg\ L^{-1}$ under 100, 50 and 10% of light intensity, respectively.	[13]
CeO_2	*Corbicula fluminea*	0.01–0.1	Genotoxicity and physiological effects using comet assay and a multienzymatic biomarker.	[14]
	Phaeodactylum tricornutum	2.5–40	Physiological and biochemical responses in 96 h growth tests in batch-culture.	[12]
	Pseudokirchneriella subcapitata	0.01–1	Median effective concentration (EC_{50}): $0.024\ mg\ L^{-1}$.	[15]
ZnO	*Ruditapes decussatus*	0.05–0.1	Biochemical and histological alterations.	[16]
	Chlorella vulgaris	50–300	Reduced lactate dehydrogenase (LDH) level at $300\ mg\ L^{-1}$ and increased glutathione content at $>100\ mg\ L^{-1}$. Lipid peroxidation increased in a dose-dependent way.	[17]
	Daphnia magna	0.25–10	LC_{50} (48 h): $1.32\ mg\ L^{-1}$ EC_{50} (24 h): $1.41 \pm 0.03\ mg\ L^{-1}$ Dose-dependent inhibition of feeding rate.	[18]
	Cyprinus carpio	50	Hyperaccumulation in liver and gill and a decrease in Na^+/K^+-ATPase activity. Inhibitory effect on SOD activity and glutathione (GSH) levels.	[19]
α-Al_2O_3 γ-Al_2O_3	*Raphidocelis subcapitana* *Daphnia magna* *Lumbriculus variegatus*	0–100	Ecotoxicity.	[20]
	Artemia salina	100	LC_{50} (96 h) $> 100\ mg\ L^{-1}$ for γ-Al_2O_3 (5 nm). α-Al_2O_3 toxic in a lesser extent. Nanoparticles (NPs) accumulated in guts.	[21]
Fe_2O_3	*Helix aspersa*	0.05–1	ROS production, lipid peroxidation, DNA integrity loss, protein carbonyl content, ubiquitin and cleaved caspases conjugates levels.	[22]
	Raphidocelis subcapitana *Daphnia magna* *Lumbriculus variegatus*	0–100	Ecotoxicity.	[20]
CuO	*Metaphire posthuma*	100–1000	Phagocytic response, generation of cytotoxic molecules, phenoloxidase, SOD, catalase, acid and alkaline phosphatase and total protein of coelomocytes.	[23]
	Brachionus plicatilis *Artemia franciscana* *Trigriopus fulvus*	0–100	EC_{50} at sub-lethal endpoints.	[24]
	Chlamys farreri	10	Released ions on the hemocytes, and ROS generation.	[25]
	Chlamydomonas reinhardtii	0.1–1000	EC_{50} (72 h): $150.45 \pm 1.2\ mg\ L^{-1}$ No observed effect concentration (NOEC) $\leq 100\ mg\ L^{-1}$ Decrease in carotenoids content (from $0.71\ \mu g\ mL^{-1}$ in control to 0.13 $\mu g\ mL^{-1}$ in $1000\ mg\ mL^{-1}$).	[26]
	Arbacia lixula	0.0007–0.02	Embryotoxicity tests and metabolic profiles.	[27]
	Mytilus galloprovincialis	1–3	Reduced growth in 68%. Copper accumulated $79.14 \pm 12.46\ \mu g\ Cu\ g^{-1}$ dry weight, higher than in control (by 60-fold).	[28]
Cu^0	*Danio rerio*	0.25–8 (25, 50 and 100 nm)	LC_{50} (25 nm): $1.07\ mg\ L^{-1}$ LC_{50} (50 nm): $2.02\ mg\ L^{-1}$ LC_{50} (100 nm): $2.39\ mg\ L^{-1}$ Inhibition of hatching and increased malformation of embryos.	[29]
	Epinephelus coioides	0.02–0.1	Time- and dose-dependent copper accumulation in tissues. Higher SOD activity, Glutathione concentration and Na^+/K^+-ATPase activity. Exacerbated apoptosis in liver and gills.	[30]
Au	*Daphnia magna*	0.2–2	Parental mortality, somatic growth and reproductive parameters.	[31]
	Ruditapes decussates	0.05–0.1	Biochemical and histological alterations.	[16]
Ag	*Oncorhynchus mykiss*	0.1	Tissue metal concentration, oxidative stress, histopathology of the blood cell and spleen.	[32]
	Allolobophora chlorotica	0–100	Survival, change in biomass and avoidance behavior.	[33]
	Hydrilla verticilata *Gambusia affinis* *Radix spp*	500	Chlorophyll content, biomass.	[34]
	Enchytraeus crypticus	25.6–2500	Lethal toxicity, reproduction toxicity, bioaccumulation.	[35]

The studies about the impact of nanoparticles (NPs) in the environment, and more specifically in sediments, sludge or soils, have been a real challenge for scientists, because their behavior, migration, possible interactions and transformations, could be completely opposite in relation to their bulk or dissolved counterparts.

Additionally, their quantification in these organic matrixes is currently difficult, principally due to technical limitations. However, recent advances have been made on this topic. Some current reports have demonstrated that single-particle inductively coupled plasma mass spectroscopy (spICP-MS) techniques could be a powerful tool for the detection of copper or silver NPs, among other MNPs/MONPs [36–38]. However, this technique could have some technical limitations for the determination of rare earth oxides NPs [39]. In this regard, the prediction and quantification of MNPs/MONPs in the environment has been based on computational models as the only mechanism to obtain information [40,41]. A general approach based on these models has suggested that soil is the main environmental compartment for the final disposal of MNPs/MONPs (8-28%), followed by water bodies (0.4–7%) and the atmosphere (0.2–1.5%) [42]. Additionally, estimations have predicted an increase of freshwater CeO_2 NPs from 1 pg L^{-1} to a few hundred ng L^{-1} by 2050, with noticeable differences depending on the type of NPs [43]. The MNPs/MONPs could enter the soil during their life cycle, through their release during their manufacture, utilization, application in bioremediation processes, or by disposal of wastes containing them as solids or sewage sludges [44–47] (Figure 1).

When the NPs enter into the soil and take part in this complex structure, a new challenge for researchers begins. The first problem to solve is the distinction of MNPs/MONPs from natural NPs and secondly, the characteristics and properties of both MNPs/MONPs (i.e. type of metal, coating, size, shape, charge) and soil (i.e. pH, ionic strength, organic matter and clay content). These intrinsic characteristics and the possible interaction between them, could affect physicochemical processes involving MNPs/MONPs transformations [41], which will certainly affect their behavior and reactivity, and concomitantly, the potential impact on the microorganisms. Some studies about individual factors and their effects have been evaluated [48–50]. However, it has been less reported about the potential effects that could cause the interplay of these individual factors. Therefore, the recent research has been a useful progress towards understanding the behavior and the effects of MNPs/MONPs in the soil. It is still a challenge to know the real levels that these tiny structures can generate in a complex and diverse soil matrix. For these same reasons, it is difficult to interpret, explain, and compare the observed differences in many studies developed in soil [8]. This is not an easy mission, considering that each soil evaluated and its respective physicochemical or microbiological characteristics, is a specific environmental condition.

Once released in soil, it is expected that MNPs/MONPs may persist for a long time period depending on the soil's characteristics, which could be a threat to beneficial microbial communities and their functionality. Consequently, some groups have researched their effects on soil microbial communities, using a mixture of parameters involving respiration, enzymatic activity, enumeration, or community structure [51–53]. The observed effects have differed depending mainly on MNPs/MONPs characteristics or soil type. It should be noted that important gaps were identified during the last few years about the effects of NPs on soil ecosystem such as the interaction with other contaminants (other metals or chemicals), aging processes and shape of NPs [41], as well as, topics scarcely studied including engineered or biogenic synthesis, or the speciation of metals [54]. Therefore, throughout this review we provide an overview of the current state of knowledge concerning exposure to MNPs/MONPs on soil and how these topics have been addressed.

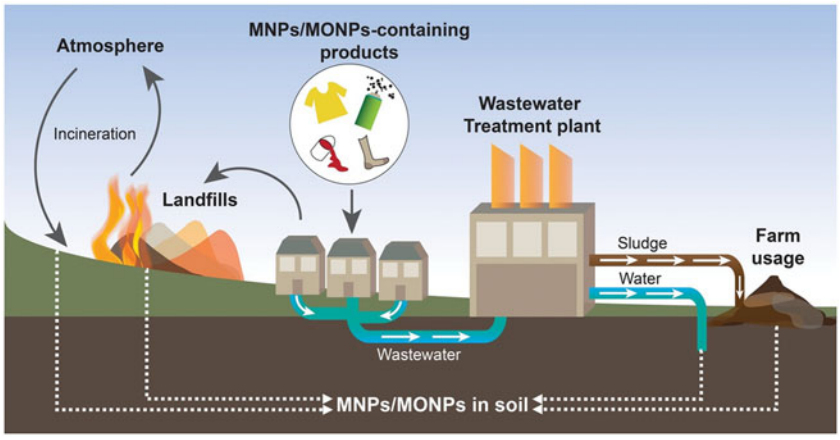

Figure 1. Main entry routes of metal (MNPs) and metal oxide nanoparticles (MONPs) into the soil from different sources.

The aim of this review is to provide basic information about hazardous implications of different classes of MNPs/MONPs (silver, gold, iron, zinc, titanium, copper, magnetite, cerium and aluminum), obtained from the assays carried out in soil microcosms, that involve studies of the impact on the structure of microbial communities, soil functionality, and biogeochemical processes mediated by microorganisms. The information provided in this study reflects the knowledge obtained during the last five years (2013–2018), which is useful to conclude if a "nano intervention" could really become a mega risk for the stability of the microbial communities and their associated biological processes. In this review, we do not cover detailed aspects on the fate or chemical transformations of MNPs/MONPs into soil, as it has been detailed by McKee and Filser [55] and by Bundschuh et al. [41]. However, a brief discussion about of soil-MNPs/MONPs interactions has been covered, because it is necessary to understand their bioavailability and potential adverse effects.

Soil-metal nanoparticle interaction

Soil has been considered as the most important sink of MNPs/MONPs and it has been proven that they can react in different forms when they reach the soil environment (Figure 2). This mainly depends on the factors related to physicochemical characteristics of MNPs/MONPs and soil [8,41,56–58]. For instance, the role of organic matter and humic substances in MNPs/MONPs stability in soil has been studied, through the capacity of the soil matrix to reduce the mobility of the NPs [59]. Consequently, alterations in the microbial population might be expected. Hadri et al. [58] evaluated the interaction of functionalized gold NPs (Au-NPs) with soil particles and concluded that the presence of natural organic matter is a key factor in their adhesion to soil, and that the concentration or surface coating does not significantly affected these interactions. Similarly, Moghaddasi et al. [49] observed that the attachment of coated and uncoated zinc oxide NPs (ZnO-NPs) in different soils was dependent on the organic matter content, but in this case, the effect was also dependent on the concentration of ZnO-NPs.

In another interesting work, Reith and Cornelis [50] evaluated the effects of soil properties on the mobility of Au-NPs and platinum NPs (Pt-NPs). Interestingly, low percentages (1–20%) of added NPs (100 μg kg^{-1}) were recovered from watery extracts, and the majority was adsorbed onto the organic matter (53–77%) and Fe/Mn-oxide (up to 42%) fractions. The authors concluded that the elevated clay content, organic carbon and Fe/Mn-oxides decreased the Au-NPs and Pt-NPs mobility and the elevated sand content increased their mobility. It should be noted that the presence of

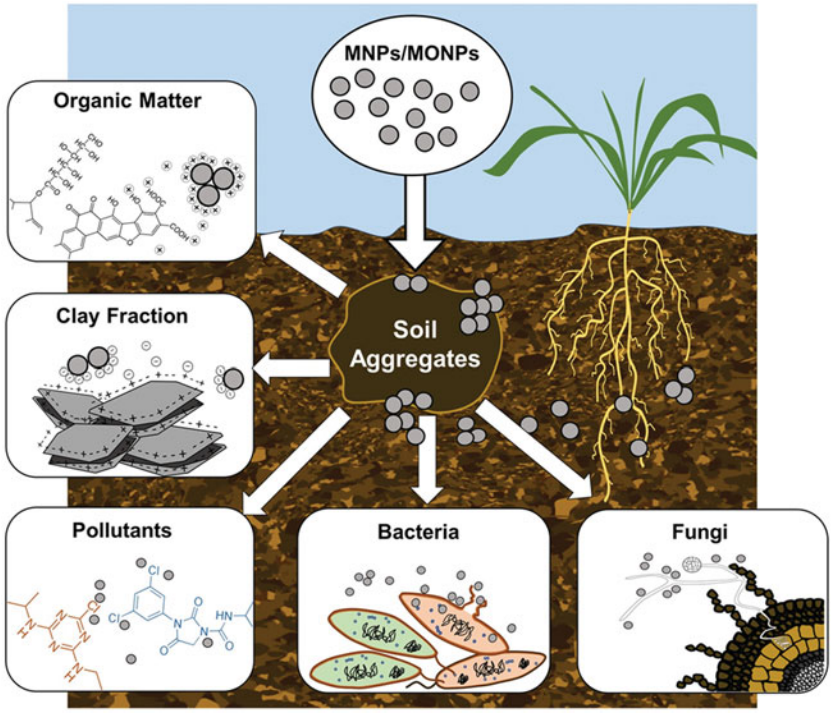

Figure 2. Main interactions produced between metal (MNPs) and metal oxide nanoparticles (MONPs) with soil components and organisms.

organic matter and humic substances represents an important nutrient source for soil microorganisms. Therefore, high concentrations of MNPs/MONPs might impose toxic effects to these microorganisms.

Nonetheless, MNPs/MONPs behavior in soil has not only been influenced by the organic matter itself, but also by different products of their decomposition such as fulvic and humic acids, which has been reported to be involved in the interface interaction mechanisms of titanium NPs (TiO_2-NPs) [60]. On the other hand, it has been suggested that pH should be considered during nanotoxicological studies [57]. These authors reported that soil zinc (as NPs or bulk) showed a strong pH-dependent effect on microbial communities, with the largest changes produced between pH 4.8 and 5.9. Contrary to this, Topuz et al. [35] reported that the bioavailability of silver NPs (Ag-NPs) was mainly affected by the organic carbon content more than the soil pH.

The surface coating, aggregation or disaggregation abilities and dissolution also may govern the behavior of MNPs/MONPs in soil, influencing their transport in water and ground waters, and consequently their deposition into soils [41,53].

Another important aspect, that must be taken into consideration, is the aging of MNPs/MONPs in soil. During an interesting work, Sekine et al. [54] reported facilitated dissolution of copper NPs (Cu-NPs) in the short time (0–5 days), and such behavior was aligned with the behavior of copper ions dissolved from a salt ($CuCl_2$) under acidic soil conditions. However, during basic conditions, dissolution was slower and copper was mainly bound to FeO(OH) or natural organic matter (NOM). Additionally, the same authors reported that in the long term (135 days), the fate of all copper forms evaluated could be probably dictated by the soil properties. In summary, the fate and possible consequences that MNPs/MONPs may have in soil due to their interactions could depend on their type, size, charge, coating or concentration, among other properties that certainly are key factors and need to be studied more carefully. Moreover, the environmental conditions (pH, organic matter content, clay or sand content) as well as the residence time in soil should be taken into consideration. Certainly, the data reported so far represents an important and relevant advance in our knowledge about the behavior of the MNPs/MONPs in soil. However, multiple questions are necessary to address future work (size of NPs, presence or absence of other metals or contaminants, interaction with amorphous clays, amongst others) in order to be aware of the risks that MNPs/MONPs accumulation involves with soil microbial communities, regarding the key role that soil microorganisms have to support the ecosystem health, biogeochemical process and the plant performance.

Silver nanoparticles

Silver NPs (Ag-NPs) have gained popularity due to their antimicrobial properties, leading to their use in many consumer products worldwide such as: clothing, food storage, cleaning products, and biomedical applications [61]. Due to this reason, it is expected an increase in the Ag-NPs concentration that could be released into the environment. In this context, the application of sewage sludge as an agricultural amendment has been mentioned as one of the major entry routes for Ag-NPs into the soil, where is suggested that they could be transformed into silver sulfides [62]. In this regard, Doolete et al. [63] evaluated the effect of Ag-NPs (44 nm), sulphidised-silver nanoparticles (Ag_2S-NPs) (152 nm) and Ag^+ (silver ion from $AgNO_3$) on soil microbial communities using metagenomic sequencing. The authors observed that hazardous concentrations of both NPs for operational taxonomic units (OTUs) were equal or lower compared to Ag^+. However, the Ag_2S-NPs were significantly less toxic when a protection level of 80% was considered for OTUs.

Other studies revealed a significant reduction in dehydrogenase and urease activities in soil exposed to 50 mg kg^{-1} of Ag-NPs (20 nm). Also, a substantial shift in bacterial community composition was observed, where Acidobacteria and Verrucomicrobiota were decreased and the Proteobacteria phylum was increased. The fungal community structure and the bacterial and archeal *amo*A gene abundance were significantly affected [64]. Similar results have been reported in soil from low artic sites, where Ag-NPs (20 nm) at 660 mg kg^{-1} caused a decrease of signature bacterial fatty acids and of the richness and evenness of bacterial and fungal DNA sequences. A decrease of 50% in microbial respiration was observed. Also, nitrogen-fixing Rhyzobiales bacteria were vulnerable to Ag-NPs [65]. The authors mentioned the importance of the particle size during toxicity studies, since Ag-NPs showed a remarkable impact on the microbial community compared to silver microparticles (3 μm). The presence of Ag-NPs (1–10 nm) at 10 and 100 mg kg^{-1} in a forest soil caused an evident decrease in microbial biomass C at both concentrations. Moreover, the authors reported an increase in the metabolic quotient, which reveals stress due to environmental changes produced by the NPs [66]. Biological activities at concentrations between

0–50 mg kg^{-1} of Ag-NPs (40 nm) were evaluated in calcareous soils with different textures and salinity levels [67]. The authors suggest that the biological effects caused by the NPs were dependent on soil type and Ag dose, since soils with low clay content were the most sensitive to Ag-NPs and no effects were observed at concentrations of <20 mg kg^{-1}.

The effect of polyvinylpyrrolidone (PVP) coated with (0.3%) Ag-NPs (30 nm) between 49 and 1815 mg kg^{-1} on biological parameters has been evaluated in a sandy loam soil by using an array of tests including: microbial respiration, enzyme activity, nitrification, molecular and physiological profiles, amongst the others [68]. The results revealed that the impact on biological parameters was evident in all the concentrations evaluated, with a half maximal inhibitory concentration (IC_{50}) as low as 20–31 mg kg^{-1}, depending on the tests applied. The effects of Ag-NPs (20 nm) on rhizosphere microorganisms has also been evaluated [69]. Interestingly, the bacterial community was more affected than the fungal cultures, and an increase in maize biomass was observed. Moreover, changes in rhizosphere were different compared to bulk soil, indicating that the rhizosphere could influence the Ag-NPs behavior. The effects of citrate-coated commercial Ag-NPs (9–10 nm) at low concentration (1 mg kg^{-1}) were evaluated on plant growth and soil microorganism community parameters [70]. Wheat plants cultured from seedlings to harvest were exposed to Ag-NPs. The composition of the soil microbial community was characterized by high throughput sequencing of 16S rRNA genes. The results showed that the NPs exposition did not inhibit wheat seed growth nor modified the seed amino acid content. The administration of Ag-NPs affected the structure of the bacterial community, particularly during the transition from seedling to the vegetative stage, affecting the soil diversity and richness. In recent work, nanocomposites of silver-graphene oxide at concentrations between 0.1–1 mg g^{-1} decreased enzymatic activities in soil up to 80%, and a similar decrease (82%) was observed during the nitrification process [71]. Although the study developed by Batista et al. [72] was mainly focused on litter decomposition, the authors reported that the effect of Ag-NPs (26–44 nm) on microbial communities was modulated by Ag-NPs or $AgNO_3$ more than by temperature. However, the negative effects were more pronounced at 10 and 23 °C. This fact emphasizes the importance in considering the temperature for the next studies about the impact of Ag-NPs in soil. Recently, evidence suggested that MNPs/MONPs can impact both microbial community composition and soil enzyme activity. However, their impact is dependent on the NPs type, concentration, shape, dissolution behavior, and chemical surface. Amongst the MNPs/MONPs evaluated, Ag-NPs (50 nm) (100 mg kg^{-1} soil) significantly inhibited soil enzyme activities [73].

The influence of spherical Ag-NPs (size of 20.4 ± 3.2 nm and zeta potential of −23.0 ± 1.0 mV) at different concentrations (0.025, 0.25 and 2.5 mg kg^{-1}) on rhizospheric microbial communities and maize (*Zea mays* L.) growth have been evaluated, and compared to bulk Ag. The results demonstrated that 2.5 mg kg^{-1} of Ag-NPs significantly reduced the dissolved organic carbon content in rhizospheric soils, and plant biomass, compared to bulk Ag. The NPs were found to accumulate in plant tissues, increasing antioxidant enzyme activity. Thus, high concentrations of AgNPs impaired plant growth and soil fertility [74].

Recently, the influence of Ag-NPs (7–14 nm) on earthworms, is considered to be a vital indicator of soil health, and tomato plants (*Lycopersicon esculentum*) were evaluated through a 72 weeks soil experiment [48]. Ag-NPs (25 and 50 mg kg^{-1}) caused severe oxidative stress in earthworms (*Eisenia fetida*). Moreover, Ag-NPs (50 ppm) decreased microbial growth in soil and nutrient availability, with significant silver dissolution being observed in the soil. Finally, the authors reported the transformation of silver into Ag_2S and Ag_3PO_4 forms, which significantly affected S and P availability.

Ecologically representative soil protozoan organisms (an environmental isolated *Acanthamoeba* strain and *Acanthamoeba castellanii* ATCC 30234 strain) were selected to evaluate the toxicity of Ag-NPs (30 and 70 nm in size) for 24 and 96 h, at concentrations from 20 to 600 mg L^{-1} [75]. A dose-dependent decrease in metabolic activity and adherence ability were observed for both strains after Ag-NPs exposure for 96 h. The authors compared the toxicity of Ag-NPs with silver ions ($AgNO_3$). Short-term exposition of protozoan organisms to $AgNO_3$ caused severe toxicity, whereas prolonged exposure led to similar effects with both $AgNO_3$ and Ag-NPs.

Biogenically synthesized Ag-NPs (2–5 nm) demonstrated potent antimicrobial activity for plant disease management without changing the microflora of the native soil, as assayed in an experimental model of *Alternaria brassicicola* and *Arabidopsis thaliana* [76]. The Ag-NPs were synthesized from a cell-free extract of *Trichoderma viride* and were found to have spherical

morphology. The activity of important soil enzymes such as urease, acid and alkaline phosphatase, dehydrogenase and β-glucosidase did not alter NPs treatment (5 μg mL^{-1}), compared to control plants. In addition, Ag-NPs did not alter the number of cultured fungi, bacteria, and actinomycetes.

It should be noted that the impact of Ag-NPs in soil microbial communities can exhibit diverse effects, since it strongly depends on several parameters, including the shape of NPs. In this context, the impact of Ag-NPs with different shapes (spheres, plates, and rods), and silver ions on bacterial toxicity and soil microbial communities have been evaluated in laboratory settings [77]. Overall, the results revealed that the microbial community was affected by changing the shape of Ag-NPs. The authors speculated Ag-NPs may change the microbial community by adversely affecting specific enzymes. Further studies are required!

Gold nanoparticles

Gold NPs (Au-NPs) may have different shapes such as triangles, rods, spheres, starts or squares, which can be used in several applications such as medicine, diagnosis and therapy, or cancer treatment. Moreover, Au-NPs associated with graphene in nanocomposites can be applied in sensors, photoelectrodes, and photocatalysis processes, among others [78]. Nonetheless, there are few studies regarding the effects of Au-NPs in soil microorganisms, and most of them refer to their low toxicity. For instance, Asadishad et al. [79] reported that commercial citrate coated (50 nm) and PVP coated Au-NPs at three concentrations (0.1, 50, and 100 mg kg^{-1}) and three particle sizes (5, 50, and 100 nm) were ecotoxically safe, and stimulatory effects on five extracellular enzymes important during nutrient cycling were observed. Moreover, an increase in Actinobacteria and Proteobacteria was observed in soil treated with citrate coated Au-NPs. Similar results were obtained by Maliszewska [80], who used biogenically synthesized Au-NPs (size of 14 ± 3 nm, zeta potential of −33 ± 3 mV) obtained from the biomass of *Streptomyces rimosus*. The impact of Au-NPs (16 and 33 mg kg^{-1} soil, after 28 days of incubation) was evaluated on microbial communities in garden soil, as assayed for community level physiological profiles and the enumeration of culturable soil microorganisms. The enzymatic activities of soil enzyme dehydrogenases: urease, alkaline phosphatase and β-glucosidase were evaluated. The results demonstrated that biogenic Au-NPs, up to the highest tested concentration, did not change the soil process, thus these nanoparticles can be considered not to be harmful.

Since it is also important to study the catabolic functions of microbial communities, Weber et al. [81] assessed the effects of Au-NPs on rhizosphere communities from *Typha* roots by using the BIOLOG ECO plate (Biolog), method commonly used to evaluate the ability of a community to utilize several kinds of carbon sources. Only a small inhibitory effect was observed at a concentration of 0.05 μg mL^{-1} and a slight positive effect on catabolic capabilities for loamy soil communities occurred. The authors finally suggested that the effect of Au-NPs on catabolic capabilities of microbial communities is minimal. Shukla et al. [82] performed *in vitro* studies to evaluate the effect of Au-NPs (∼45 nm) on the growth of plant growth promoting rhizobacteria (PGPR). In detail, Au-NPs at 6.25 mg L^{-1} provoked 63% acceleration of growth in *Paenibacillus elgii*, 57% in *Pseudomonas fluorescens,* and 33% in *Bacillus subtilis* while *Pseudomonas putida* was unaltered. Accordingly, the authors conclude that Au-NPs may be used for the development of nano-biofertilizers.

As can be seen from the literature during the last years, Au-NPs have been one of the less evaluated in soil microbial community studies. Therefore, future studies should be focused about Au-NPs impact in soil, as their use in medical application and environmental release will increase unavoidably.

Iron and iron oxides nanoparticles

Iron is one of the most abundant elements in the earth crust and is ubiquitous in many biogeochemical compartments [83]. Zero-valent Iron, Iron Oxide, and Magnetite NPs (ZVFe-NPs, FeO-NPs and Fe_3O_4-NPs, respectively) are mainly used as an effective tools to remediate pollution in soil through reductive transformations and detoxification of many contaminants [45,84]. There is currently no detailed information regarding their impact on soil microbial communities. However, during the last five years, some research groups have shed light about their potential effects. The iron crystal structure, along with NPs size, charge, solubility and presence of organic matter molecules are reported to impact the NPs reactivity and thus, their toxicity [83]. In addition, the cytotoxic effects of iron-based NPs towards bacteria are associated with oxidative stress through generation of ROS. These effects might lead to the interplay of oxygen with reduced iron species or from the disturbance of the ionic transport chain due to the affinity of cell membranes to the NPs [6,83].

For instance, Shah et al. [85] reported that according to results obtained with pyrosequencing, ZVFe-NPs in soil (size range of 2–58 nm at 550 mg kg^{-1}) did not cause significant changes in bacterial communities. Also, the impact observed could be more attributed to environmental parameters more than to the presence of the NPs. Quasi-spherical FeO-NPs (10.0 ± 2.5 nm) at concentrations of 1 and 10 mg kg^{-1} soil demonstrated, in contrast to Ag-NPs, positive effects on N and C cycles, evidenced by increased microbial metabolic activity and nitrification potential [86]. As discussed by the authors, this phenomenon could be attributed to the role of iron as an essential micronutrient involved in microbial metabolism and biochemical reactions such as nitrate synthesis, nitrogen fixation or DNA synthesis.

ZVFe-NPs concentrations as high as 1000 or 2000 mg kg^{-1} have been evaluated in soil and the results demonstrated that 1000 mg kg^{-1} (to be used in rhizoremediation processes) did not cause negative effects on microbial parameters, but did cause indirect toxic effects on plant root elongation [87]. Conversely, when 2000 mg kg^{-1} were applied, heterotrophic cultivable bacteria, fungal colonies, microbial biomass carbon and nitrogen mineralization were significantly decreased after 180 days of incubation [88].

On the other hand, Fe_3O_4-NPs have been widely used in biomedical applications, mainly due to their biocompatibility beneficial characteristics [89]. Nonetheless, some studies have reported their impact on the soil environment: Antisari et al. [51] evaluated the effect of Fe_3O_4-NPs on microbial biomass, and their availability through soil particles. The results showed an increase on microbial C/N ratio from 8 in the control to 17 at the lowest rate of Fe_3O_4-NPs evaluated (10 mg Kg^{-1}) in the first week and on a metabolic quotient after 60 days, which represents microbial stress and changes produced in the bacterial/fungal biomass ratio, according to the authors. Besides, it was evidenced through cellular lyses with the $CHCl_3$ method that Fe was taken up by soil microorganisms from NPs dissolution, whereas Fe_3O_4-NPs showed a low solubility. In fact, they formed small aggregates in soil. Based on these results, the authors concluded that studies of diversity on microbial communities, as well as the type of interaction between NPs and organic or inorganic compounds need to be understood, for a better comprehension of the risks about NPs in the soil. Moreover, it has been reported that the effect of Fe_3O_4-NPs may vary according to the soil type. In relation to this, Frenk et al. [90] observed a harmful and higher effect of Fe_3O_4-NPs on microbial communities in a sandy loam soil compared to sandy clay soil, through changes in bacterial composition and hydrolytic activity. In contrast, no effects were observed in the sandy clay soil.

Cao et al. [91] investigated the impact of quasi-spherical Fe_3O_4-NPs (10.2 ± 2.6 nm), synthesized by the co-precipitation technique, on arbuscular mycorrhizal (AM) community, and fungi/plant soil ecosystems. Using a greenhouse pot experiment, *Zea may L.* growth and AM fungal community was monitored following administration of Fe_3O_4-NPs (0.1, 1.0, and 10.0 mg kg^{-1}), and compared with bulk Fe_3O_4. The authors observed that the highest tested concentration of Fe_3O_4-NPs was toxic to AM fungi by impairing their diversity, and changing their community structure, in comparison with bulk Fe_3O_4. Therefore, particulate Fe_3O_4 might deteriorate the nutrient provision of AM fungi for maize, impairing soil fertility.

Zinc, zinc oxide and titanium oxide nanoparticles

During the last years, Zinc, Zinc Oxide, and Titanium Oxide NPs (Zn-NPs, ZnO-NPs and TiO_2-NPs, respectively) have been extensively used in cosmetics such as sunscreens, plastics, and paints. Moreover, these NPs have been applied in the remediation of contaminated soil and water [92–94]. Studies carried out with ZnO-NPs and TiO_2-NPs in soil have reported contrasting results about the effects of these NPs on microbial communities or biological activities. In this regard, Shen et al. [95] evaluated the fluorescein diacetate hydrolyzing and dehydrogenase activities and the ammonification as ecotoxicological parameters in different soils exposed to ZnO-NPs (10–300 nm) at concentrations between 1000 and 10000 mg kg^{-1} of soil. The ammonification was significantly modified from 1000 mg kg^{-1} and all enzyme activities, as well as the respiration parameters, were negatively affected by the presence of ZnO-NPs. However, the toxicity was strongly correlated with pH: a higher negative impact on acidic or neutral soils and a lower impact on alkaline soils. According to the authors, this could be explained by the influence of pH on the ionic dissolution ZnO-NPs. The effects of commercial ZnO-NPs (58.40 ± 30.13 nm) at 1000 mg kg^{-1} on soil microbes and their soil functions on Date palm (*Phoenix dactylifera*) were evaluated [96]. The administration of ZnO-NPs on litter-amended soil decreased the fungal and bacterial colony forming units, compared to control. Zn was detected in the microbial biomass upon nanoparticles administration in soil, suggesting an uptake and accumulation of ZnO-NPs into the cell cytosol of the microorganisms. Overall,

ZnO-NPs were toxic to microbe soil, affecting their carbon and nitrogen mineralization.

Similar results were found by Chai et al. [97] where a reduction in *Azotobacter,* P-solubilizing, K-solubilizing bacteria and enzyme activity in soil was observed following the addition of ZnO-NPs at the same concentration. A negative impact on beneficial soil microorganisms and on the production of plant growth promoting substances has been reported [98]. After exposure to increased concentrations of ZnO-NPs, the cell viability of *P. aeruginosa*, *P. fluorescens* and *B. amyloliquefaciens* decreased significantly as well as the production of indole acetic acid. Contrary to this, Sindhura et al. [99] reported that the addition of Zn-NPs did cause alteration of enzymatic activity in soil or of microbial activity. Moreover, an increase in biological activities and physiological parameters of the plants has been observed.

Recently, Xu et al. [100] evaluated the effects of commercial ZnO-NPs (size of 90 nm) and bulk ZnO at different concentrations (0, 1, 10, 100 mg kg^{-1}), on the growth of *Lactuca sativa* L. and their impact on the associated rhizospheric soil bacterial community. The authors reported [100] that NPs or bulk material, at concentrations of 10 mg kg^{-1}, modified the soil bacterial community structure. In addition, some lineages within the *Cyanobacteria* showed a similar or different response towards bulk ZnO and ZnO-NPs, as demonstrated by their taxonomic distribution. The results indicated that distinct microbial processes occurred in soil as a result of the treatments.

The long-term effects (56 d) of commercial ZnO-NPs (<50 nm) was evaluated at concentrations of 50 and 500 mg kg^{-1} on the activities of soil exoenzymes in planted soils (acid phosphatase, fluorescein diacetate (FDA) hydrolase, β-glucosidase, urease, dehydrogenase, and arylsulfatase) [101]. The study was performed by using the Organization for Economic Co-operation and Development (OECD) standard soil. Except for FDA hydrolase activity, significant effects (increase or decrease of enzymatic activity) were reported for all the studied enzymes. The main conclusions were that ZnO-NPs at 50 and 500 mg kg^{-1} might adversely affect soil enzymes, mainly urease and acid phosphatase, which may compromise the nitrogen and phosphorous cycles in the soil. Zinc might interact with sulfhydryl moieties at the active sites of enzymes, such as urease, decreasing catalytic activity.

The impact of commercial ZnO-NPs (50 nm) and TiO_2-NPs (100 nm) in various soils was evaluated by using the Phytotoxkit F^{TM} method [102]. The results demonstrated that both nanoparticles affected the growth of *Lepidium sativum* roots, however no impact on seed germination was reported. The toxicity was evaluated during contact time between soil and the NPs, along with the effects of temperature and light. ZnO-NPs were found to be more toxic in comparison to TiO_2-NPs. In addition, a reduction of NPs toxicity was found during increased temperature and aging, while enhanced toxic effects were observed under light conditions. The authors assumed that the increased temperature and extended contact time of NPs with soil (aging). This might enhance the interactions of the NPs with soil components and reduce the negative effects of the NPs due to the formation of complexes between Zn and organic matter. They conclude that the impact of NPs in plants is caused by several factors that control the NPs-soil-plant system. Also, further studies are required to better understand this relation by considering the use of various soil types.

Alterations in soil microbial communities have also been observed after the addition of TiO_2-NPs. Moll et al. [103] reported that TiO_2-NPs (of 29 and 92 nm) caused alterations in prokaryotic communities but not in fungal communities. Interestingly, these authors reported that the composition of the prokaryotic community, evaluated by Illumina Miseq (16S or ITS2 regions), was different during treatment with NPs, bulk zinc (> 100 nm) and control without NPs. This indicates that the response of microbial communities to TiO_2-NPs could be regulated by the NPs size. Simonin et al. [104] evaluated the effects of TiO_2-NPs (21 nm) at 1 and 500 mg kg^{-1} in soil. These authors reported that even at the lowest concentration, TiO_2-NPs had a negative impact on the nitrification activities and the abundance of ammonia-oxidizing microorganisms after 90 days of exposure. A study carried out in soil columns evaluated the effects of TiO_2-NPs applied as a single (50 mg L^{-1}) or repeated exposure (two of 25 mg L^{-1} or three of 16.5 mg L^{-1}) on the abundance and activity of soil nitrifying microbial communities after two months of incubation. The results demonstrated that under repeated exposures the addition of NPs was more harmful to soil microorganisms [105]. Soil exposition to concentrations of <200 mg kg^{-1} of undoped or nitrogen-doped TiO_2-NPs (40–60 nm ms) did not cause alterations in the microbial composition of maize or soybean rhizosphere. However, both NPs caused a negative impact on arbuscular mycorrhizal fungi [106]. Conversely, no effects on arbuscular mycorrhizal fungi or biological nitrogen fixation by rhizobia were observed in a soil amended with TiO_2-NPs (~29 nm) at concentrations between 100 and 1000 mg kg^{-1} [107].

More sensitive microorganisms as nitrifying bacteria or archaea have been affected by TiO_2-NPs in soil. However, a non-classical dose-response was found by Simonin et al. [107]. The authors evaluated concentrations between 0.05 and 500 mg kg^{-1} and reported that the archaea abundance was reduced by 40% with all the concentrations evaluated. Moreover, whilst no effect was found in the *Nitrospira* abundance, *Nitrobacter* was affected (25% reduced nitrification) at 0.05 mg kg^{-1}, and the highest concentrations (100 and 500 mg kg^{-1}). In relation to soil properties, it has been reported that the toxicity of TiO_2-NPs is more related to soil pH and organic matter content, more than the soil texture itself [8]. More recently, Huang et al. [108] reported that TiO_2-NPs (8–25 nm) in the presence of metalaxyl did not cause significant changes in biomass or the bacterial community regardless of the metalaxyl concentration.

Copper and copper oxides nanoparticles

Copper and Copper Oxide NPs (Cu-NPs and CuO-NPs, respectively) have raised great interest due to their beneficial characteristics such as high thermal and electrical conductivity, lubrication, catalyst, and low cost [109–111] whereby, they have been included in many consumer products. However, some studies have reported on their impact regarding soil microorganisms. Frenk et al. [89] evaluated the harmful impact of different concentrations of CuO-NPs on the bacterial community activity of two soil types. They concluded that a sandy loam (SL) soil was more affected than a sandy clay loam (SCL) soil due to the stronger effect of CuO-NPs on bacterial hydrolytic activity, community, composition, and oxidative potential. Even when the SCL soil was affected in a lesser extent, the oxidative potential was significantly reduced and the community composition changed. The abundance of bacteria from *Bacilli* class was reduced after 0.1% and 1% CuO-NPs exposure for SL and SCL soil, respectively. *Rhizobiales* and *Sphingobacteriaceae* were also negatively affected. The authors discussed the probability of clay and organic matter content interacting with CuO-NPs, consequently the toxicity might have decreased. The effects of CuO-NPs on microbial communities associated with salt marsh plants (*Pragmites australis* and *Halimione portulacoides*) rhizosphere were evaluated and compared with ionic Cu [112]. CuO-NPs and ionic Cu significantly changed the microbial community, suggesting that CuO-NPs might cause disturbances in ecosystem functions. The impact of commercial CuO-NPs (40 nm) at different concentrations (0,100,500, and 1000 mg kg^{-1} soil) on microbes in a flooded paddy soil was evaluated and compared to TiO_2-NPs (20 nm) [113]. CuO-NPs demonstrated higher negative effects on soil microbes compared to TiO_2-NPs, as indicated by a decrease in soil microbial biomass and important soil enzymatic activities (phosphatase, urease, and dehydrogenase). In addition, due to the superior dissolution of CuO-NPs, these NPs affected soil microbes by impairing nutrient bioavailability and increasing oxidative stress.

The impact of CuO-NPs on the bacterial soil community was compared to Fe_3O_4-NPs (both of $<$50 nm) [114]. The results demonstrated the superior toxicity of CuO-NPs to soil bacterial communities, as assayed by denaturing gradient gel electrophoresis fingerprinting.

In this regard, Shah et al. [53] reported that the high organic carbon content in soil could increase the retention time of Cu-NPs and ions in the soil and therefore, a high impact on microbial communities was produced. Moreover, the same authors reported that soil pH could have a strong influence on the fate of Cu-NPs in soil and consequently on microbial communities. They reported that Cu-NPs (10–100 nm) in an acidic soil caused changes in the overall bacterial community richness, and Cu-NPs showed high rates of transformation to ions and adsorption to soil through the complex formulation. According to the above discussion, alkaline, neutral or acidic conditions should be considered in studies with NPs in the soil. Moreover, under more realistic environmental conditions, a rhizosphere soil could have a stronger influence on the dissolution and toxicity of Cu-NPs compared with bulk soil [115], and therefore, different effects on soil microbial communities could be expected.

In another study, Zhai et al. [116] evaluated different shapes and sizes of MNPs/MONPs and their dissolution potential on the metabolic potential of soil bacteria. Interesting results showed that although the size of NPs is important in relation to antimicrobial properties, the shape should be considered. For example, spherical Cu-NPs (500 nm) were more toxic to soil microbial communities than rod-shaped Cu-NPs (78 nm), which would be related to their morphology and dissolution capacity (ion release).

Cerium and aluminum oxide nanoparticles

Cerium and Aluminum Oxide NPs (Al_2O_3-NPs and CeO_2-NPs, respectively) have several applications. For example, CeO_2-NPs have been involved in bio-sensing and biomedical applications [117,118] and as an antimicrobial agent [119]. The Al_2O_3-NPs have been studied as an additive to biodiesel-diesel blends, to enhance the rheological and filtration properties of fluids or as

antimicrobial agents [120–122]. Their toxic effects on the environment have been evaluated mainly on plants, aquatic organisms, terrestrial invertebrates, or individual bacteria [123–126]. However, studies about their impact on the soil have been reported during the last five years. For instance, Moll et al. [127] evaluated the effects of CeO_2-NPs (50 nm) at 400 mg kg^{-1} on symbiotic microorganisms in soil with a cover of red clover. The authors reported insignificant effects on mycorrhizal fungi or rhizobia.

Li et al. [128] evaluated whether commercial CeO_2-NPs (25 nm) might affect soil fertility and quality by modifying the enzymatic activity of soil enzymes. The study was performed in a soil-grass microcosm system, and the authors measured the specific enzymatic activity of three soil enzymes (β-glucosidase, phosphatase, and urease). CeO_2-NPs at concentrations of 0, 100, 500, and 1000 mg kg^{-1} soil mixture were applied in individual pots with organic hard red wheat (*Triticum aestivum*). CeO_2-NPs at concentrations of 100 and 1000 mg kg^{-1} inhibited β-glucosidase and urease activities, and stimulated the phosphatase activity. In addition, the authors reported that the aging of CeO_2-NPs alleviated their impact on soil enzymes, decreasing their toxicity [128].

On the other hand, little information exists about the negative effects of Al_2O_3-NPs on microbial communities, even when Al_2O_3-NPs (50 nm) have been applied at high concentrations (5000 mg kg^{-1}) [129]. Similar results were found by McGee et al. [64], where Al_2O_3-NPs (20–30 nm) did not cause major changes at 50 mg kg^{-1} in the microbial community structure or to enzyme activities. In this sense, the impact of Al_2O_3-NPs on fungal and bacterial communities in agricultural pastureland soil was evaluated by molecular fingerprinting and enzyme analysis and compared with the impact of Ag-NPs. Overall, Al_2O_3-NPs (50 mg kg^{-1}) had no effects on microbial communities (both bacterial and fungal composition).

It is noticeable that the scarce information about the soil impact of Al_2O_3-NPs and CeO_2-NPs, compared with the rest of MNPs/MONPs mentioned in this review, even when the second are considered as one of the most used worldwide, especially in medicine [130]. Indeed, according to a report of the Grand View Research Inc., global CeO_2-NPs production is expected to reach US$1.04 billion by 2025 [131].

Conclusions and perspectives

It is evident from the reviewed literature that the majority of MNPs/MONPs may disturb negatively biological processes in soil, due to the fact that many bacterial groups have been susceptible to their exposure. In addition, they can significantly influence the enzymatic activities of important soil enzymes and thus, change the soil bacterial community [132]. However, further research should be focused on Ag-NPs, Cu-NPs, and TiO_2-NPs, because they have been demonstrated to cause a more severe stress in a dose-dependent way. The scarce information about the effects produced by Al_2O_3-NPs and CeO_2-NPs is not a sufficient basis to conclude if their presence in soil may be a risk for the microbial communities. The information provided about Au-NPs and Fe_2O_3-NPs in this review indicates that their exposure has not led to severe effects on soil microbial communities, and conversely, stimulatory effects on biological activities have been observed.

It is known that the impact of MNPs/MONP, produced on microbial communities, has mainly been influenced by the soil properties. Specifically, pH and organic carbon content, more than soil texture, have been identified as the main factors. Although some studies have also suggested the clay content is an important factor in this process. However, the specific mechanisms involved in the low or high toxicity of MNPs/MONPs have been uncertain so far, whereby more efforts should be devoted to a better understanding.

On the other hand, even when the toxic effects of some MNPs/MONPs on soil invertebrates and microorganisms have been demonstrated, it has scarcely considered the influence that the presence of others compounds co-existing in soil may have. In relation to this, it has been suggested that persistent pollutants (*e.g.* pesticides) interacting with metals such as copper or cadmium could intensify or alleviate their toxicity. Therefore, the antagonistic or synergistic interaction potentially produced between MNPs/MONPs and other contaminants should be explored, in order to simulate realistic conditions for soil contamination. In this regard, it is necessary to evaluate more chronic exposure scenarios (repeated applications of MNPs/MONPs) under more realistic concentration conditions of both NPs and other contaminants.

Despite the reported changes on the diversity of microbial communities and the impact of beneficial bacteria in various soil types exposed to MNPs/MONPs, the scarce research about the response of ecological processes mediated by bacteria, fungi or actinobacteria is noticable. Although there has been progress in recent years, and evidence for acute biodiversity changes derived from MNPs/MONPs is still limited. Important questions about their effect in the long term remain

unanswered. As mentioned before, several MNPs/MONPs can change with aging, and then it is possible to ask when will these changes affect negatively or positively microbial communities? Will microbial communities adapt to the presence of more toxic MNPs/MONPs in soil over time? Or could the interaction of MNPs/MONPs with the soil components be permanent over time? It is still necessary to answer these and other questions and to have the complete scenario about the real magnitude (nano or mega risk) of the impact of metal nanoparticles on soil microbial communities.

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